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THE DETERMINATION OF ARSENIC IN URINE.

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SOME years ago one of us (S.) had occasion to make a number of analyses of urine in cases of suspected chronic arsenical poisoning.¹ In looking up the literature of the subject at that time, it was found that the analysis of the urine in case of chronic arsenical poisoning had been comparatively rare. In the twenty-three cases cited by Sanger in which the urine had been examined and the methods of analysis described, the latter were generally open to adverse criticism. They were usually tedious and often involved the use of many reagents, thereby adding to the possibility of introduction of arsenic. The amounts of arsenic found, in the absence at that time of any method for the determination of small quantities, could only be judged from the descriptions of the mirrors, but probably did not exceed 1 mg. of arsenious oxide per liter, and in many cases must have been less than 0.1 mg. In the only analysis found in which quantitative results were given, the amount was stated to have been 16.8 mg. in 1700 c.c., but the method of analysis was not given, hence this case was not included in the twenty-three above mentioned.

The method used by Sanger for the treatment of the urine was based on that proposed by Gautier² for the general treatment of animal tissue. To a measured volume of urine was added about one tenth the volume of concentrated nitric acid, and the whole was evaporated over a free flame. As the mass neared dryness the flame was lowered, and more acid was added, if necessary, in order to avoid carbonization at the end. Deflagration often ensued, but it was thought that loss of arsenic should not be feared in presence of excess of nitric acid. To destroy the organic matter completely, the residue from evaporation was transferred to a smaller dish, treated with sulphuric acid, and heated for some time, with addition of nitric acid, until a clear, white, partly melted mass was obtained. The residue, free from nitric acid,

¹ These Proceedings, **29**, 148 (1894).

² Ann. d. Chim. et d. Phys., [5] **8**, 384 (1876); Bull. Soc. Chim., [2] **24**, 250 (1875).

was diluted with water and introduced into the Marsh flask. The amount of arsenic was determined by Sanger's³ modification of the Berzelius-Marsh method.

In the twenty cases of suspected arsenical poisoning referred to in the above paper, thirty-one samples of urine were examined by this method, and in no instance was the amount of arsenic (as arsenious oxide) greater than 0.07 mg. per liter. The analytical precautions were such as to preclude the introduction of arsenic from any outside source. Prior to these analyses but one instance had been found in which a method for the quantitative estimation of arsenic in urine had been described. Hubbard,⁴ in studying the elimination of arsenic by the kidneys, added the urine directly to the Marsh flask and determined the weight of the mirror according to the gravimetric Berzelius-Marsh method, first applied by Gautier,⁵ and afterwards elaborated by Chittenden and Donaldson⁶ and others. While the amounts of arsenic found by Hubbard (varying from 0.35 to 1.12 mg. per liter) were undoubtedly a close approximation, the method cannot be applied to minimal amounts with certainty on account of the impossibility of accurately weighing small mirrors and the effect of the presence of organic matter on their deposition.

The treatment described above has been used by several analysts⁷ in the determination of arsenic in urine. Unfortunately it was not accurately tested by the analysis of urines containing known amounts of arsenic, partly on account of lack of time, partly through acceptance of the Gautier method. The assumption that all of the arsenic present was accounted for was probably incorrect, as our present work will show.

The method is a troublesome one, requiring much time for evaporation and the destruction of the organic matter, as care must be taken to have the latter entirely eliminated, since the accurate determination of the arsenic is impossible in its presence. The use of large quantities of nitric acid is unpleasant and may introduce error. These considerations, together with the much more important one of possible loss of arsenic, have led us to substitute for the destruction of the organic matter with nitric acid a distillation of the arsenic from the evaporated urine by means of hydrochloric acid.

³ These Proceedings, **26**, 24 (1891); Amer. Chem. Jour., **13**, 431 (1891).

⁴ Physician and Surgeon, Ann Arbor, Mich., **4**, 348 (1882); Contr. Chem. Lab. Univ. Mich., **1**, Part I (1882).

⁵ Loc. cit.

⁶ Amer. Chem. Jour., **2**, 235 (1881).

⁷ Putnam-Worcester, Bost. Med. Surg. Jour., **124**, 623 (1891); Wood, Ibid., **128**, 414 (1893); and others.

The distillation of arsenic from organic matter by hydrochloric acid, first used successfully by Schneider⁸ and Fyffe,⁹ is a common procedure and needs no explanation. We have not been able, however, to find any instance of its application to the analysis of urine. The only serious objection is the difficulty of obtaining hydrochloric acid with a negligible amount of arsenic. Fortunately such an acid is obtainable at low cost in this country,¹⁰ and one does not have to resort to the troublesome methods of purification, which to some are prohibitive of the use of hydrochloric acid in arsenic work.

Not only is the distillation method more accurate, but it will also be shown that, in point of time for the entire operation, the advantage is greatly in its favor, particularly, as we have said before, if the careful elimination of the organic matter is made a prerequisite to the introduction of the solution into the Marsh flask.

THE METHOD.

Apparatus. For distillation, a 300 c. c. round-bottom flask is used, with a neck about 20 cm. long. The side tube, which is about half-way up the neck, is 20 cm. in length, and is bent downward in the middle at an obtuse angle, so that it passes into an upright condenser parallel to the neck of the boiling flask, which is closed by a short glass tube sealed off at each end, over which is slipped a short piece of rubber tubing. A glass-stoppered boiling flask could advantageously be used. The cooling tube is 50 cm. long, with a jacket of 35 cm. The side tube of the flask passes through a rubber stopper in the neck of the condenser and as far into the cooling tube as possible. The condensing tube passes at the bottom through a rubber stopper, over which is slipped a wide tube 15 cm. long, similar to a chloride of calcium tube, having a bulb of about 25 c.c. capacity near the lower end, which terminates in a tube of ordinary bore. To this end is fused a tube of equal diameter about 15 cm. long. The arrangement is practically a pipette-shaped adapter, similar to that used in ammonia distillation, and is intended to prevent the rise of distillate into the condenser in case of back pressure. The distilling apparatus is conveniently set up in duplicate, mounted on two stands (see Figure A), and is placed in the hood under a strong draught.

Distillation. 200 c.c. of urine are evaporated in a porcelain dish over a low flame or on the steam bath to about 35 c.c., cooled, and in-

⁸ Pogg. Ann., **85**, 433 (1851).

⁹ Jour. f. prakt. Chem., **55**, 103 (1852).

¹⁰ Baker and Adamson Chemical Company, Easton, Pa.

roduced into the flask, which is then connected with the condenser. Under the adapter is placed a small flask containing 25 c.c. concentrated nitric acid, which should just cover the end of the adapter. There are then added, through a long funnel tube, 100 c.c. cool, con-

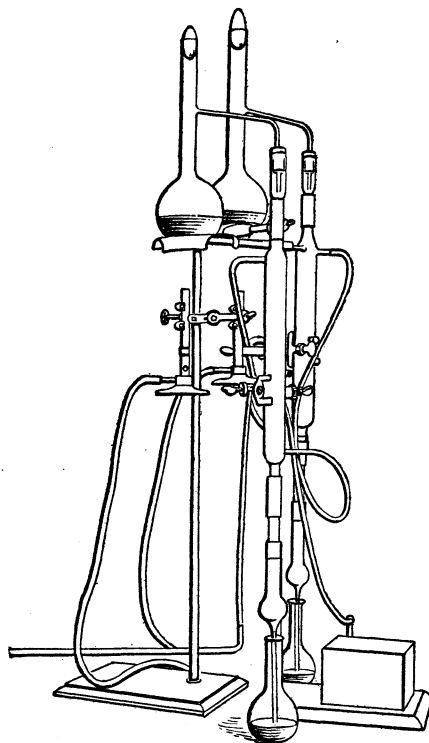


FIGURE A.

centrated hydrochloric acid, in which the amount of arsenic is as small as possible and accurately determined. The stopper of the flask is at once inserted.

Distillation is begun with a low flame and is continued at such a rate that the volume of the liquid in the flask is reduced to about half in the course of thirty to forty minutes. Repeated trials have shown that all the arsenic, in the quantities for which this method is intended, goes over by this operation, whether the arsenic is present as arsenious or arsenic acid. As by far the greater part of the arsenic goes over

with the gaseous hydrochloric acid and meets the concentrated nitric acid, no loss is to be feared from the dilution of the nitric acid by the acid distillate. Comparatively little organic matter is distilled, and this is entirely destroyed by the subsequent procedure.

Treatment of the Distillate. To the distillate are added 25 c.c. concentrated nitric acid, in order to decompose completely during evaporation any excess of hydrochloric acid and thus guard against loss of arsenic. The mixture is then evaporated to a small bulk, three to five cubic centimeters of concentrated sulphuric acid added, and the evaporation continued until the nitric acid is expelled. To destroy the slight amount of organic matter which usually remains, a few drops of nitric acid are added, and the heating is continued until only the small residue of sulphuric acid is left, which must be colorless. The residue is then diluted with water to a measured volume of about 25 c.c., or, if preferred, to a quantity which is weighed in a side-neck test tube to the second decimal place.

Determination of the Arsenic. The subsequent procedure, as in the paper above referred to, follows closely the method of Sanger¹¹ for determining small amounts of arsenic, except that the capillary tube should be cooled at the deposition point of the mirror, as advised by Gautier,¹² Thomson,¹³ Lockemann,¹⁴ and others. An aliquot portion of the ultimate solution, accurately measured or weighed, is introduced into the Marsh flask, the entire apparatus having been in action for a sufficient time to show absence of arsenic. This time varies according to the importance of the test in hand, but should not be less than twenty minutes. If, after the addition of the solution, a mirror does not make its appearance in the capillary tube within ten minutes, a larger portion or the whole of the solution is added. After the appearance of the mirror the heating of the tube is continued for a sufficient time to insure the complete deposition of the arsenic, which usually occurs within an hour. During this time the flow of hydrogen is regulated by the constant generator, so that the height of the flame at the end of the heated tube is about one millimeter, the regular deposition of the mirror being dependent on this condition. The mirror obtained is compared with a set of standards, which is prepared as explained in the paper referred to. From the amount of solution used and the

¹¹ Loc. cit.

¹² Bull. Soc. Chim., [2] **27**, 1030 (1902.)

¹³ Chem. News, **88**, 228 (1903).

¹⁴ Zeitschr. f. angew. Chem., **18**, 416 (1905).

volume of urine taken, the quantity of arsenic per liter is calculated. Should the mirror exceed in size the standard of 0.06 mg., it may be necessary to obtain another mirror from a smaller portion of the solution or from a smaller volume of urine, since the reading of mirrors above 0.06 mg. is not accurate.

The determination of the amount of arsenic in the solution may also be made by the modification of the Gutzeit method described by us in the preceding paper.¹⁵ In this case, owing to the size of reduction flask used, the volume of the solution should not exceed 20 c.c., of which an aliquot part or all may be taken. This method consists briefly in allowing the arsenical hydrogen to pass through a tube containing a strip of paper saturated with a five per cent solution of mercuric chloride and dried. The resulting band of color is compared with a set of standard bands.

Reagents. The zinc used, known as Bertha spelter, from the New Jersey Zinc Company of New York, has been used in this laboratory for many years, and has been exhaustively tested for arsenic with negative results. It contains not over 0.013 per cent of iron and not more than 0.019 per cent of lead. The amount taken is from five to ten grams. We have used it in a rather finely granulated form in the reduction bottle, reserving the larger pieces for the constant generator. As the metal is too pure to generate hydrogen with sufficient rapidity from sulphuric acid, we place in the reduction bottle a thin disk of platinum foil nearly as large as the bottom of the bottle. With this the evolution of the hydrogen is most regular. That the platinum does not cause arsenic to be held back, we have assured ourselves by obtaining mirrors of equal size and same appearance as those formed without the disk. The deposition of platinum on the zinc by use of platinic chloride is, however, not allowable, as one of us has shown,¹⁶ and cupric sulphate is equally inadmissible. The formation of a coating of copper on our zinc, after the procedure of Lockemann,¹⁷ does not add to its sensitiveness, nor does the addition of tin or lead salts to the solution during reduction. In the constant generator, the zinc is sensitized, according to the suggestion of Gooch,¹⁸ by treatment with a solution of cupric sulphate, but we take the precaution to pass the hydrogen from the generator through a ten per cent solution of

¹⁵ These Proceedings, **43**, 297 (1907); Jour. Soc. Chem. Ind., Vol. **26** (1907); Zeitschr. f. anorg. Chem., Vol. **56** (1907).

¹⁶ Loc. cit., p. 39.

¹⁷ Loc. cit.

¹⁸ Amer. Jour. Science, [3] **48**, 292 (1894).

cupric sulphate in order to retain any hydrogen sulphide which may be formed.

The sulphuric acid is from the Baker and Adamson Chemical Company, and has never shown a trace of arsenic when tested in greater quantity and for a longer time than in a single determination. In the constant generator it is used at a dilution of 1 to 8 ; in the reduction bottle somewhat more dilute (1.5 normal).

The hydrochloric acid is also obtained of the Baker and Adamson Company. Two grades¹⁹ have been used : the ordinary chemically pure acid (A), which was found by repeated trials to contain 0.4 mg. arsenious oxide per liter ; and a second (B), in which we have determined by careful analysis an amount equal to 0.02 mg. per liter.

The nitric acid is an ordinary, chemically pure acid, tested in large quantity after evaporation with sulphuric acid and found to be entirely free from arsenic, both by the Marsh and Gutzeit tests.

Utensils. All glass and porcelain vessels were new, and, after freedom from arsenic was assured by blank tests, were reserved for this purpose alone.

ANALYTICAL RESULTS.

Blank Tests. 1. 100 c.c. hydrochloric acid (A) were diluted with 35 c.c. water and distilled into 25 c.c. nitric acid. From the evaporated distillate a mirror was obtained equal to 0.04 mg. arsenic.²⁰ Amount per liter, 0.4 mg.

2. 100 c.c. acid (A) were added, drop by drop, to 50 c.c. hot nitric acid in a porcelain dish. The mixture evaporated with sulphuric acid gave a mirror equal to 0.04 mg. arsenic. Amount per liter, 0.4 mg.

3. 100 c.c. hydrochloric acid (B) were diluted with 35 c.c. water and distilled into 25 c.c. nitric acid. The evaporated distillate gave a mirror which was judged to be about 0.003 mg. arsenic.

4. 200 c.c. acid (B) were added, drop by drop, to 100 c.c. hot nitric acid and the resulting mixture evaporated with sulphuric acid until the nitric acid was expelled. From this was obtained a mirror which was read as 0.002 mg. arsenic.

From analyses 3 and 4 it was evident that there was a trace of

¹⁹ A third grade (C) has been obtained from the same source since the completion of the analytical work on this paper. In this acid, which is of exceptional purity, the amount of arsenic is not over 0.004 mg. per liter.

²⁰ In these analyses "arsenic," unless otherwise specified, means arsenious oxide.

arsenic in the acid (B), probably about 0.002 mg. in 100 c.c. or 0.02 mg. per liter.

5. 300 c.c. urine were evaporated to 30 c.c. and distilled with 100 c.c. hydrochloric acid (A) into 25 c.c. nitric acid. One half of the solution from the evaporated distillate gave a mirror equal to 0.02 mg. arsenic; the other half, a color band (Gutzeit) equal to 0.02 mg. The amount of arsenic per liter is therefore 0.4 mg., which confirms the results of analyses 1 and 2, and the test shows the urine to be free from arsenic.

6. 200 c.c. urine were evaporated to 30 c.c., and distilled with 100 c.c. acid (B) into 25 c.c. nitric acid. The distillate, evaporated with a little more nitric acid, gave a mirror which, as nearly as could be judged, was equal to 0.002 mg. This confirms, within the limits of reading, the results of analyses 3 and 4, and enables us to fix the correction for 100 c.c. of this acid at 0.002 mg. This has been since confirmed by the analysis of the acid by the Gutzeit method. The correction is only appreciable, as will be seen from Series B, below, when the entire solution gives a very low mirror, and entirely disappears when the mirror, even if a low one, is obtained from a small part of the solution (see Series C).

The third grade of hydrochloric acid (C), which will hereafter be used in all urine work in this laboratory, was tested as in analyses 2 and 4. After reduction of the residues from two lots of 100 c.c. with sulphurous acid, color bands were obtained equal to 0.3 and 0.5 micro-milligrams (0.001 milligram) of arsenic. This is equivalent to 0.004 mg. arsenic per liter. The correction for 100 c.c. of this acid, 0.0004 mg., would be practically inappreciable under ordinary conditions of the Marsh procedure, even if the mirror was obtained from the entire solution.

Analyses. For use in the subsequent analytical work, a solution of arsenious acid was made as follows: One gram of pure arsenious oxide, twice resublimed, was dissolved in a small amount of sodic hydroxide free from arsenic. After acidification with sulphuric acid, this solution was made up to a liter. Of this, 10 c.c. were diluted to a liter, giving a solution containing 0.01 mg. arsenious oxide to the cubic centimeter.

7. 150 c.c. urine, to which had been added 0.025 mg. arsenic, were evaporated to 25 c.c. and distilled with 100 c.c. hydrochloric acid containing 0.035 mg. arsenic. The total amount was 0.06 mg. 25 c.c. of distillate were collected in 25 c.c. nitric acid, and from this was obtained a mirror equal to 0.06 mg. 50 c.c. more of the distillate were collected in 15 c.c. nitric acid, and from this no mirror was found.

8. By the same procedure as in analysis 7, and also with 150 c.c. urine, 25 c.c. distillate gave 0.06 mg. arsenic, equal to the amount taken. 50 c.c. additional distillate gave no mirror.

9. With 200 c.c. urine and the same amount of arsenic, the same procedure gave 25 c.c. distillate containing 0.06 mg. arsenic, and 50 c.c. additional distillate yielded no further mirror.

The results of analyses 7, 8, and 9 show that by distilling one half the contents of the flask, according to the method above described, all the arsenic passes over.

The following series shows that by the former method of destroying the organic matter by evaporation with nitric acid a very large error is made :

SERIES A.

NITRIC ACID METHOD.

No. of Analysis.	Volume of Urine taken.	As ₂ O ₃ added.	As ₂ O ₃ recovered.	Per cent recovered.
	c.c.	mg.	mg.	
10	500	25.0	6.0	24
11	500	2.5	0.44	18
12	300	0.3	0.00	0
13	100	0.5	0.00	0

In analyses 10 and 11, actual deflagration took place; in Nos. 12 and 13 the residues were blackened.

The next series, B, p. 336, gives the results of a preliminary trial of the distillation treatment, and shows that by the distillation method very small amounts of arsenic can be recovered with practical completeness. As a more severe test of the method, 0.01 mg. arsenic was added to a liter of urine and the analysis carried out as usual, using acid B (Analysis 39). A mirror was obtained fully equal to the standard for 0.01 mg.

Even with the correction for this acid, we thus recover from 80 to 100 per cent of the amount of arsenic taken, which shows that, considering the amount of organic matter involved and the hydrochloric acid used, the method is a delicate one. By the use of an acid of such purity as that of grade C, it will be possible to eliminate entirely the correction for arsenic in the acid, even if the amount of arsenic in the

SERIES B.

DISTILLATION METHOD.

No. of Anal- ysis.	Volume Urine taken.	As ₂ O ₃ added.	As ₂ O ₃ in 100 c.c. HCl.	Total As ₂ O ₃ taken.	As ₂ O ₃ recovered.	Per cent recovered.
	c.c.	mg.	mg.	mg.	mg.	
16	200	0.10	0.04	0.14	0.14	100
17	"	0.15	"	0.19	0.16	80
18	"	0.05	"	0.09	0.09	100
19	"	0.15	"	0.19	0.16	80
20	"	0.20	"	0.24	0.24	100
Average per cent recovered, Nos. 16 to 20						92
38	"	0.07	0.002	0.072	0.077	107
37	"	0.06	"	0.062	0.06	97
36	"	0.04	"	0.042	0.04	95
35	"	0.03	"	0.032	0.03	94
34	"	0.02	"	0.022	0.02	91
33	"	0.01	"	0.012	0.01	83
Average per cent recovered, Nos. 38 to 33						95

entire test solution is as low as 0.01 mg., since the correction is only four per cent of this quantity, which is well within the limit of accuracy of the method itself. With larger amounts than 0.01 mg. the correction for this acid is of course of even less account.

Presence of Arseniates in the Urine. The compound in which arsenic occurs in the urine has never to our knowledge been thoroughly investigated. To determine accurately the condition of such small amounts as would ordinarily occur would be a matter of considerable difficulty. Schmidt and Bredtschneider²¹ claim to have found arsenic acid and

²¹ Moleschott's Untersuchungen, 6, 146 (1859).

no arsenious when arsenic was ingested as the trioxide. Selmi²² states that he found in the urine of a dog poisoned by arsenic a volatile compound of the element. The reference gives no analytical details and the original is not accessible to us. It is not improbable, however, from the analogy to phosphorus, that arsenic finds its way into the urine as an arseniate. If this be the case, the question will perhaps be asked if small amounts of arseniate, when distilled with hydrochloric acid, would be recovered in the distillate or would require a preliminary reduction before distillation.

Mayerhofer²³ has shown that if arsenic acid is distilled with a sufficiently large quantity of hydrochloric acid, it is converted to arsenic trichloride, chlorine being given off, since the pentachloride does not exist under ordinary conditions. In our method the concentration of the hydrochloric acid in 100 c.c. of its solution would be so great compared with that of the arseniate that a complete conversion to trichloride might be predicted. That this is the case is shown by the following analyses, in which the arsenic acid used was prepared by evaporating a measured quantity of arsenious acid solution to dryness with nitric acid before adding to the urine.

SERIES C.

DISTILLATION METHOD IN PRESENCE OF ARSENIATES.

No. of Analysis.	Volume Urine taken.	As ₂ O ₃ added, as H ₃ AsO ₄ .	As ₂ O ₃ in 100 c.c. HCl.	Total As ₂ O ₃ taken.	As ₂ O ₃ recovered.	Per cent recovered.
	c.c.	mg.	mg.	mg.	mg.	
40	200	0.25	0.002	0.252	0.25	99.2
41	"	0.50	"	0.502	0.50	99.6

Analyses of Urine. The method was finally tested by the analysis of six samples of urine to which varying amounts of arsenic had been added by one of us, the amounts not being known to the analyst.

²² Mem. d. Accad. d. Scienze, Bologna, [4] 1, 299 (1882) ; ref., Gazz. Chim. Ital., 12, 558 (1882).

²³ Ann. Chem. u. Pharm., 158, 326 (1871).

SERIES D.

DISTILLATION METHOD.

No. of Analysis.	As ₂ O ₃ per Liter.	Volume Urine taken.	As ₂ O ₃ present in Volume taken.	Total As ₂ O ₃ in Volume taken.	As ₂ O ₃ found in Volume taken.	Corrected (Correction, 0.04 mg.)	As ₂ O ₃ found per Liter.	Per cent found.
	mg.	c.c.	mg.	mg.	mg.		mg.	
21	0.5	200	0.10	0.14	0.15	0.11	0.55	110
22	2.0	"	0.40	0.44	0.38	0.34	1.70	85
23	1.0	"	0.20	0.24	0.23	0.19	0.95	95
24	1.5	"	0.30	0.34	0.33	0.29	1.45	97
25	0.8	"	0.16	0.20	0.17	0.13	0.65	81
26	1.2	"	0.24	0.28	0.28	0.24	1.20	100
Average per cent found								95

To show the calculation of the analysis, one example will suffice :

No. of Analysis.	Volume Urine taken.	Volume of Solution used.	Volume of Solution taken.	Reading of Mirror.	Reading of Mirror, Average.
	c.c.	c.c.	c.c.	mg.	mg.
26	200	50	5	a) 0.025 b) 0.030	0.028
Amount in solution taken, 10×0.028 = 0.28 mg.					
Less correction for HCl 0.24 "					
Amount per liter urine, 5×0.24 = 1.2 "					

Comparison of Methods. In order to compare more fairly the distillation method with the method of evaporation, the latter was slightly modified to secure the most favorable conditions for the recovery of the arsenic. 200 c.c. urine were evaporated to about 50 c.c., and then treated with 25 c.c. concentrated nitric acid and 5 c.c. sulphuric acid. Evaporation was continued until the fumes of sulphuric acid appeared, which left a dark residue containing a large amount of organic matter. By successive addition of small amounts of nitric acid and heating,

this residue was oxidized after a very long time, so that it appeared nearly colorless. The diluted residue was then added to the reduction bottle. A series of analyses was made by this method in which the amounts of arsenic were not known to the analyst.

SERIES E.

NITRIC ACID METHOD, MODIFIED.

No. of Analysis.	As ₂ O ₃ per Liter.	Volume Urine taken.	As ₂ O ₃ present in Volume taken.	As ₂ O ₃ found in Volume taken. (Corrected.)	As ₂ O ₃ found per Liter.	Per cent found.
	mg.	c.c.	mg.	mg.	mg.	
27	0.8	200	0.16	0.13	0.65	81
28	1.0	"	0.20	0.08	0.40	40
29	0.5	"	0.10	0.10	0.50	100
30	2.0	"	0.40	0.24	1.20	60
31	1.2	"	0.24	0.12	0.60	50
32	1.5	"	0.30	0.18	0.90	60
Average per cent found						65

From comparison of Series D and E, it will be seen that the distillation method is more accurate than the evaporation method, even if the latter is carefully conducted so that the loss from carbonization is avoided as far as possible. But the time needed for a proper treatment with nitric acid by the latter method is very great, and the manipulation uncleanly. The entire preparation of the solution for testing, in the distillation method, does not consume more than three fifths of the time required in the other, and the procedure is much cleaner.

USE OF THE METHOD.

We have not studied the question of how small an amount of arsenic can be recovered from the urine by this method, but have been content to show that very small amounts, even as little as 0.01 mg. per liter, can be detected and estimated with reasonable accuracy. (Series A and Analysis No. 39.) For the examination of abnormal urine, — in studying the elimination of arsenic through the kidneys, for instance, — it would be seldom necessary to consider a quantity

smaller than 0.01 mg., although the delicacy of the Marsh and Gutzeit methods permits a fairly exact estimation of much smaller amounts. If the question of the occurrence of arsenic in normal urine is to be investigated, — and we hope that opportunity for such an important study may be found at some future time in this laboratory, — the delicacy of the methods is secondary in importance to that of the source and manner of collection of the urine. The absolute delicacy of the Marsh method is claimed by Thomson²⁴ to be 0.0004 mg. of arsenious oxide, by Lockemann²⁵ and others, 0.0001 mg. arsenic, and we have been able to recognize by our modification of the Gutzeit method as little as 0.00008 mg. of arsenious oxide. But until it is shown that a urine has had absolutely no arsenical contamination, such extreme delicacy is apt to be misleading.

The use of the method in the analysis of other liquids containing organic matter suggests itself, for example in the more exact determination of arsenic in beer. Although the distillation of small quantities of arsenic from animal tissue with hydrochloric acid has been rejected by Lockemann²⁵ and others, either on account of the amount of arsenic in commercial, pure acid, or the difficulty of purifying the acid, yet we believe that the distillation of organic matter with acid of only 0.004 mg. arsenic to the liter would not introduce a serious error into an investigation of the normal occurrence of arsenic in the organs of man.

HARVARD UNIVERSITY, CAMBRIDGE, MASS., U. S. A.,
August, 1907.

²⁴ Loc. cit.

²⁵ Loc. cit.